

PATENT SPECIFICATION

DRAWINGS ATTACHED

L138.750



L138.750

Date of Application and filing Complete Specification: 6 Oct., 1966.
No. 44743/66.

Application made in Netherlands (No. 6513 426) on 16 Oct., 1965.
Complete Specification Published: 1 Jan., 1969.

© Crown Copyright 1969.

Index at acceptance:—C2 C2B36

Int. Cl.:—C 07 c 83/02

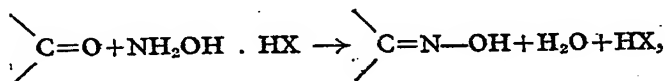
COMPLETE SPECIFICATION

Preparation of Oximes

We, STAMICARBON N.V., a Netherlands Limited Liability Company of 2 van der Maesenstraat, Heerlen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of oximes by reaction of a C_4-C_6 -ketone particularly cyclohexanone, and a solution of a hydroxylammonium salt in water.

According to the reaction equation:



15 where

20 C=O represents the carbonyl group of the cyclic ketone and HX any given acid, it will be seen that the acid which is bound in the hydroxylammonium salt is liberated during the oxime formation.

25 A complete conversion of ketone into oxime can be achieved in a medium varying from weakly acid to neutral, and the acid liberated in the oxime formation being bound by addition of a neutralizing agent, usually gaseous ammonia or ammonia water. This technique results however in the formation of a salt. When hydroxylamine is introduced as hydroxylammonium sulphate, the salt thus produced is ammonium sulphate.

30 To reduce the production of salt in such reactions it has been proposed to carry out the reaction in a buffered medium, using a solution of a hydroxylammonium salt derived from a weak acid, the reaction mixture also containing a soluble salt of the said weak acid in such an amount that during the oxime formation this salt, together with the liberated acid, form a buffered reaction medium the pH of which is sufficiently high to allow the formation of oxime to proceed.

[Price 4s. 6d.]

45 Upon completion of the oxime formation and isolation of the oxime formed, the salt of the weak acid is separated from the solution, which insofar as the hydroxylammonium salt is concerned does not react further, and the separated salt fed back into the reaction medium in which the oxime formation takes place, while the remaining solution of the weak acid, which now has a low salt content, is used either in a hydroxylamine synthesis stage to convert hydroxylamine into hydroxylammonium salt, or for other acid-consuming purposes.

50 A process of this type has the disadvantage that the salt of the weak acid has to be repeatedly separated from the reacted solution, which is expensive. Another unattractive feature is the fact that it is economically necessary to recycle the isolated solid salt to the reaction medium.

55 It has now been found that in such buffered reaction processes the steps of isolating the salt from the reacted solution, and the recycling of this salt to the reaction medium, can be omitted if the ketone is dissolved in a water-immiscible i.e., water insoluble, or slightly water-miscible, organic solvent in which the oxime formed readily dissolves, and is brought into intimate counter-current con-

BEST AVAILABLE COPY

tact with an aqueous solution of a hydroxylammonium salt derived from a weak acid, which aqueous solution also contains an amount of a soluble salt of the weak acid which, together with the acid liberated in the oxime formation, forms the buffer medium.

The invention therefore consists of a process for the preparation of an oxime, which comprises contacting in a reaction zone in counter-current flow a stream of a solution of a C_4-C_8 cyclic ketone in an organic solvent therefor, the said solvent being water-insoluble, or having a solubility in water of less than 0.1% by weight at 20°C, and which is a solvent also for the oxime reaction product; and a stream of an aqueous solution of the hydroxylammonium salt of an acid having a dissociation constant of from 2×10^{-1} to 10^{-6} , the said aqueous stream containing a further soluble salt of the said acid to provide, with free acid produced in the reaction zone, a buffered reaction medium; and withdrawing from the reaction zone a product stream of oxime dissolved in the said solvent therefor, and an aqueous stream containing free acid and the soluble salt thereof; separating solvent from the said product oxime; and recycling the solvent thus obtained to the said reaction zone.

Particularly suitable organic solvents for use in the process of the invention include inexpensive solvents such as toluene, benzene, methylcyclopentane and cyclohexane.

The weak acids to which the hydroxylamine is bound in the form of hydroxylamine salt in the aqueous starting solution must, while being sufficiently weak to produce, together with a salt derived from them, such a buffering effect that the pH is kept sufficiently high for making the oxime formation proceed also be sufficiently strong to be capable of forming the hydroxylammonium ion with dissolved hydroxylamine.

While theoretically these requirements are met by acids and acidic salts having a dissociation constant of 2×10^{-1} to 10^{-6} . However, in practice only the readily obtainable and consequently cheap, inorganic acids, such as phosphoric acid and ammonium or alkali-metal bisulphate, (which can be regarded as an acid), are in fact acceptable for this purpose. If the cyclic ketone is brought into counter-current contact with the hydroxylammonium salt solution in the presence of the organic solvent, a relatively high degree of conversion of the ketone into the oxime is achieved even at very low pH-values, for example from 0 to 1.

In carrying out the oxime preparation according to the invention use may be made of the normal type of counterflow reactors, such as columns filled with packing bodies or rotating disc reactors, provided that the ketone-containing organic phase is sufficiently

finely distributed when it is contacted with the water phase containing the hydroxylammonium salt. A fine distribution can be promoted by pulsating the liquid flow.

The reaction can also be carried out as a counter-flow reaction in a system consisting of a number, e.g. 3 to 6, of series-connected reactors equipped with stirrers, each of these reactors also being provided with a liquid-liquid separator.

The starting solution containing the hydroxylammonium salt can be directly obtained in a hydroxylamine synthesis in which nitrate ions or NO are either electrolytically or with the aid of molecular hydrogen in the presence of a noble metal catalyst, reduced to hydroxylamine in a buffered acid medium. The aqueous solution which, so far as hydroxylamine is concerned, does not react further and has to be discharged during the oxime preparation can, after removal of traces of organic solvent and non-converted ketone, be recycled to such a hydroxylamine synthesis.

Owing to the presence of the organic solvent, the process according to the invention has the additional advantage that the oxime formed dissolves in the said solvent, while substances which are discharged together with this oxime if no organic solvent is present, such as the weak acid contained in the reaction mixture, are left in the aqueous phase. After the organic solvent has been separated off by distillation, an oxime is left, which can be processed into the corresponding lactam.

Two embodiments of the invention are hereinafter described and schematically illustrated in the accompanying drawings.

According to the embodiment shown in Figure 1, the oxime preparation is carried out in a counter-current reactor A, at one end of which the aqueous solution containing the hydroxylammonium salt of the acid together with a soluble salt of the weak acid, is supplied through conduit 1, while at the other end the cyclic ketone and the organic solvent are supplied through the conduits 2 and 3, respectively.

When these starting liquids flow in counter-current relationship through the reactor A, the ketone is converted into oxime, which dissolves in the organic solvent. The oxime-containing organic solvent is, (preferably after being washed with water or dilute ammonia to remove traces of acid salts from it), fed through conduit 4 to a rectifying column C provided with a heating spiral 5. The oxime thus separated is discharged from this rectifying column via conduit 6, while the evaporated solvent is, after being condensed, fed to an extraction plant B via conduit 7 to free the aqueous solution discharged from counter-flow reactor A via conduit 8, from any ketone and oxime still dissolved therein. The acid

BEST AVAILABLE COPY

aqueous solution thus obtained is discharged via conduit 9. Any solvent dissolved in this solution is recovered by stripping.

The embodiment shown in Figure II differs from that according to Figure I, in that the stream of organic solvent discharged from counter-flow reactor A, in which solvent non-converted ketone is still present, is, together with an amount of hydroxylammonium salt solution supplied via conduit 11, fed into an after-reaction vessel D provided with a stirrer 10 to convert the ketone still present into oxime at a pH which has been raised with the aid of an alkaline reagent supplied via conduit 12. The reaction mixture flows via conduit 13 into a liquid-liquid separator E, after which the supernatant layer (i.e. the organic solvent in which ketone is dissolved) is fed to column C, while the water layer flows into counter-current reactor A via conduit 15.

The process according to Figure I can be used if a virtually complete conversion of ketone into oxime is directly achieved in counter-flow reactor A. The process according to Figure II may be applied if the conversion of ketone into oxime in counter-flow reactor A is incomplete.

The degree of conversion depends on the pH in the reaction medium and particularly on the pH of the reacted aqueous solution discharged from the counter-flow reactor via conduit 8. If the said pH is below about 0.5, further reaction at a raised pH will be required to achieve a virtually complete conversion of ketone into oxime.

In a preferred embodiment of the process according to the invention equimolecular amounts of ketone and hydroxylammonium salt are reacted per unit time. However, owing to the counter-flow circulation, a large excess of hydroxylammonium will be present with respect to ketone still to be converted when the hydroxylammonium salt solution enters the counter-flow reactor, which is favourable for achieving a satisfactory degree of conversion. The acid aqueous solution which, as far as hydroxylammonium salt is concerned, does not react further and has to be discharged from the system via conduit 9, can be advantageously fed to a hydroxylamine synthesis stage to serve as the reaction medium and to provide the acid required for binding the hydroxylamine formed as hydroxylammonium salt.

The following examples of the invention are provided:

EXAMPLE I

This is an example of the preparation of cyclohexanone oxime by reaction of a buffered hydroxylammonium phosphate solution and cyclohexanone in the presence of toluene.

Using the process according to Figure I, the following hydroxylammonium salt solution

was fed to counter-current reactor A via conduit 1, per unit time:

65 kmols of $\text{NH}_2\text{OH} \cdot \text{H}_3\text{PO}_4$,

97 kmols of $\text{NH}_4\text{H}_2\text{PO}_4$,

38 kmols of H_3PO_4 ,

191 kmols of NH_4NO_3 and

3184 kmols of H_2O

The said solution was derived from a hydroxylamine synthesis stage in which nitrate ions, supplied in the form of 55% by weight of nitric acid, were reduced to hydroxylamine with the aid of hydrogen in a medium buffered with the aid of a combination of phosphate and phosphoric acid and in the presence of a platinum catalyst. The pH of the solution was 2.1.

A further solution of 65 kmols of cyclohexanone, and a toluene stream containing:

400 kmols of toluene,

9 kmols of cyclohexanone,

2 kmols of oxime and

5 kmols of H_2O .

were admitted to the said reactor A via the conduits 2 and 3, respectively.

The temperature in the reactor A was maintained at 70°C.

An oxime-containing toluene product stream was discharged from the reactor through conduit 4 to column C. The said product stream contained:

400 kmols of toluene,

65 kmols of oxime and

20 kmols of H_2O .

In column C, separation into oxime and toluene was effected. 65 kmols of oxime per unit time were discharged via conduit 6, while toluene (400 kmols) and water (20 kmols) were discharged to extraction column B via conduit 7.

An aqueous solution was discharged per unit time via conduit 8 to extraction column B containing:

191 kmols of NH_4NO_3 ,

97 kmols of $\text{NH}_4\text{H}_2\text{PO}_4$,

103 kmols of H_3PO_4 ,

9 kmols of cyclohexanone,

2 kmols of oxime and

3234 kmols of H_2O .

Which solution, as far as the hydroxylammonium salt is concerned, does not react further and which has a pH of 1.0.

After removal of toluene dissolved therein by stripping, the aqueous solution discharged from extraction column B had the following composition:

97 kmols of $\text{NH}_4\text{H}_2\text{PO}_4$,

191 kmols of NH_4NO_3 ,

103 kmols of H_3PO_4 and

3249 kmols of H_2O .

This solution was recycled to the hydroxylamine synthesis stage to serve as the reaction medium in the reduction of nitric acid to hydroxylamine.

If, in contrast to the process according to the invention, cyclohexanone and a hydroxyl-

BEST AVAILABLE COPY

ammonium salt solution having the same composition as the one described in Example I is made to flow countercurrently in the absence of the organic solvent, an oxime-containing phase which comprises 1.25% by weight of cyclohexanone, 5.75% by weight of water and 0.63% by weight of phosphoric acid, will be obtained. This indicates that the oxime-forming reaction has not proceeded to completion and that the oxime obtained still contains a considerable proportion of water, so that prior to its rearrangement to caprolactam, the oxime will either have to be dried or more SO_2 will have to be used in the said rearrangement. Moreover, the phosphoric acid in the reaction product is lost from the reaction.

A further disadvantage is that the water phase to be discharged will contain about 2.7% by weight of cyclohexanone. This non-converted cyclohexanone will have to be stripped from the solution and recycled to the oxime reactor.

EXAMPLE II

This is an example of the preparation of cyclohexanone oxime by reaction of cyclohexanone and a hydroxylammonium sulphate solution obtained by catalytic reduction of NO with the aid of hydrogen in a medium buffered with mono-ammonium phosphate and phosphoric acid.

Using again the process according to Figure I, the following hydroxylammonium salt solution was fed to reactor A via conduit 1, per unit time:

65 kmoles of $\text{NH}_2\text{OH} \cdot \text{H}_3\text{PO}_4$,
40 kmoles of $\text{N}_2\text{H}_4\text{PO}_4$,
25 kmoles of H_3PO_4 and
1000 kmoles of H_2O .

The said solution had a pH of 2.5, and was obtained by the catalytic reduction of NO with H in a medium buffered with ammonium phosphate and phosphoric acid.

65 kmoles of cyclohexanone and a toluene stream containing:

200 kmoles of toluene,
10 kmoles of cyclohexanone,
1 kmole of oxime and
5 kmoles of H_2O .

were fed into the said reactor A via the conduits 2 and 3, respectively.

An oxime-containing toluene product stream consisting of 65 kmoles of oxime, 200 kmoles of toluene and 10 kmoles of H_2O , together forming an organic phase, were discharged from this reactor per unit time via conduit 4 and fed to column C, and therein separated into an oxime stream (65 kmoles) discharged as the product via conduit 6, and a toluene-water mixture (200 kmoles of toluene, 10 kmoles of water) discharged to extraction column B via conduit 7.

An aqueous phase containing 40 kmoles of $\text{NH}_4\text{H}_2\text{PO}_4$, 90 kmoles of H_3PO_4 , 10

kmoles of cyclohexanone, 1 kmole of oxime and 1060 kmoles of H_2O , and having a pH of 1.5, was discharged from reactor A to extraction column B, via conduit 8. The cyclohexanone and the oxime dissolved in the water phase were removed therefrom by extraction with the supplied toluene stream.

After removal of the dissolved toluene by stripping, the solution discharged via conduit 9 contained: 40 kmoles of $\text{NH}_4\text{H}_2\text{PO}_4$, 90 kmoles of H_3PO_4 and 1065 kmoles of H_2O . This solution can be used as the reaction medium in the catalytic reduction of NO to hydroxylamine with the aid of hydrogen, and can to this end be fed to such a hydroxylamine synthesis reactor.

EXAMPLE III

This is an example of the preparation of cyclohexanone oxime, starting from cyclohexanone and a hydroxylammonium sulphate solution buffered with the aid of ammonium sulphate and ammonium bisulphate.

Because of the higher acidity of the hydroxylammonium sulphate solution ($\text{pH} \approx 0-0.5$) as compared with the hydroxylammonium salt solutions referred to in the two previous examples which had a pH of from 1 to 2, the reaction was carried out by the process according to Figure II.

The following solution was introduced via conduit 1 per unit time to one end of the reactor A,

80 kmoles of $\text{NH}_2\text{OH} \cdot \text{NH}_4\text{SO}_4$,
99.2 kmoles of NH_4HSO_4 ,
1.28 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
10.4 kmoles of NH_4NO_3 ,
960 kmoles of H_2O .

The following solution was also introduced into the same end of reactor A via conduit

1 kmole of $\text{NH}_2\text{OH} \cdot \text{NH}_4\text{SO}_4$,
44.12 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
2.6 kmoles of NH_4NO_3 ,
379 kmoles of H_2O .

At the other end of reactor A, 100 kmoles of cyclohexanone, and a benzene stream containing 260 kmoles of benzene, 10 kmoles of cyclohexanone and 6 kmoles of H_2O , were supplied via the conduits 2 and 3, respectively.

A benzene stream containing 260 kmoles of benzene, 81 kmoles of oxime, 19 kmoles of cyclohexanone and 10 kmoles of H_2O was discharged from reactor A to the subsequent reactor D, to convert the cyclohexanone still present in the said benzene stream into oxime at a pH of 4.5 and a temperature of 60°C , together with hydroxylammonium salt solution supplied via conduit 11, the said salt solution having the composition:

20 kmoles of $\text{NH}_2\text{OH} \cdot \text{NH}_4\text{SO}_4$,
24.8 kmoles of NH_4HSO_4 ,
0.32 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
2.6 kmoles of NH_4NO_3 .

A solution comprising 240 kmoles of H_2O

and 25.6% by weight of ammonia water, corresponding to 43.8 kmoles of NH_3 and 120 kmoles of H_2O , was supplied via conduit 12 to reactor D. The reaction mixture flowed from the said reactor D into the liquid-liquid separator E. The oxime-containing benzene layer, consisting of 100 kmoles of oxime, 10 kmoles of H_2O and 260 kmoles of benzene, was discharged from this separator and fed to column C, in which separation was effected between the oxime product (100 kmoles), which was discharged via conduit 6, and a benzene stream (260 kmoles of benzene and 10 kmoles of H_2O), which was discharged to extraction column B via conduit 7. The water layer formed in separator E was fed to reactor A via conduit 15.

The aqueous phase had a pH of about 0 and the composition

- 180.2 kmoles of NH_4HSO_4 ,
- 45.4 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
- 13.0 kmoles of NH_4NO_3 ,
- 10.0 kmoles of cyclohexanone and
- 1416 kmoles of H_2O .

It was discharged from reactor A through conduit 8 and fed into extraction column B. Upon extraction therein by the benzene stream, followed by stripping off the dissolved benzene, an aqueous reaction solution was discharged through conduit 9 consisting of 180.2 kmoles of NH_4HSO_4 , 45.2 kmoles of $(\text{NH}_4)_2\text{SO}_4$, 13.0 kmoles of NH_4NO_3 and 1420 kmoles of H_2O .

Upon further neutralization with NH_3 , this solution can be processed into ammonium sulphate.

WHAT WE CLAIM IS:—

1. A process for the preparation of an oxime, which comprises contacting in a reaction zone in countercurrent flow a stream of a solution of a C_4 — C_6 cyclic ketone in an organic solvent therefor, the said solvent being water-insoluble, or having a solubility in water of less than 0.1% by weight at

20°C, and which is a solvent also for the oxime reaction product; and a stream of an aqueous solution of the hydroxylammonium salt of an acid having a dissociation constant of from 2×10^{-1} to 10^{-6} , the said aqueous stream containing a further soluble salt of the said acid to provide, with free acid produced in the reaction zone, a buffered reaction medium; and withdrawing from the reaction zone a product stream of oxime dissolved in the said solvent therefor, and an aqueous stream containing free acid and the soluble salt thereof; separating solvent from the said product oxime; and recycling the solvent thus obtained to the said reaction zone.

2. A process as claimed in Claim 1, in which the said weak acid is phosphoric acid, ammonium bisulphate or alkali-metal bisulphate.

3. A process as claimed in Claim 1 or Claim 2, in which the solvent recovered from the said product stream is contacted with the said aqueous stream from the reaction zone to extract residual ketone and/or oxime contained in said aqueous stream.

4. A process as claimed in Claim 3, in which the said hydroxylamine salt of a weak acid is obtained by reduction of nitrate ions or NO in a buffered solution comprising the said extracted aqueous stream.

5. A process as claimed in any of Claims 1 to 4, in which reaction in the reaction zone is effected with equimolecular streams of ketone and hydroxylammonium salt per unit time.

6. A process for the preparation of an oxime as claimed in Claim 1, substantially as hereinbefore described.

7. An oxime prepared by a process claimed in any of the preceding claims.

HYDE & HEIDE,
110, Bishopsgate,
London, E.C.2.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.

Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

BEST AVAILABLE COPY

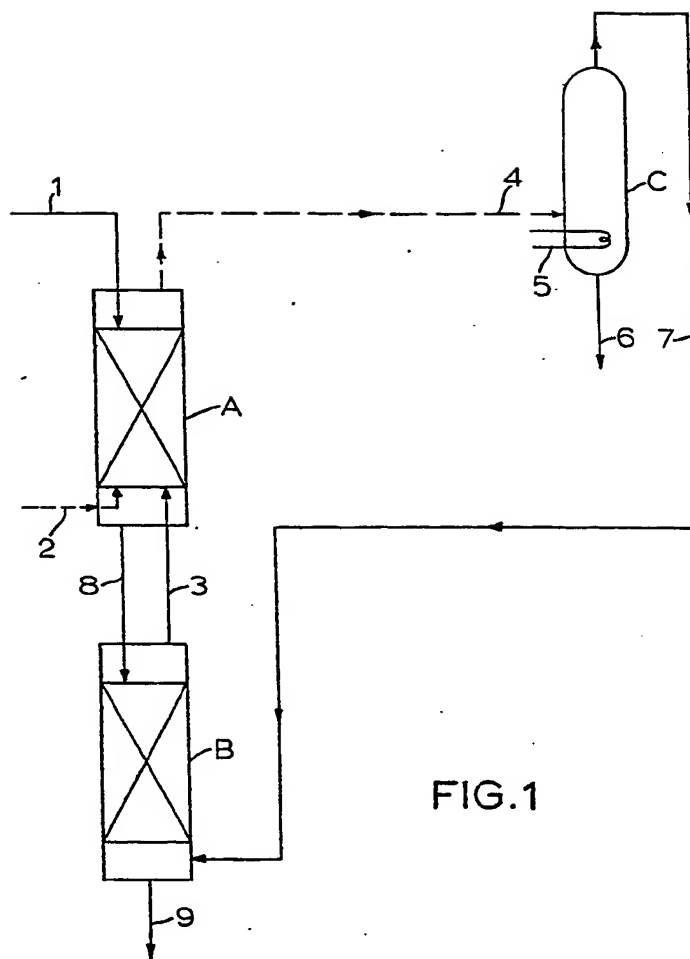


FIG.1

BEST AVAILABLE COPY

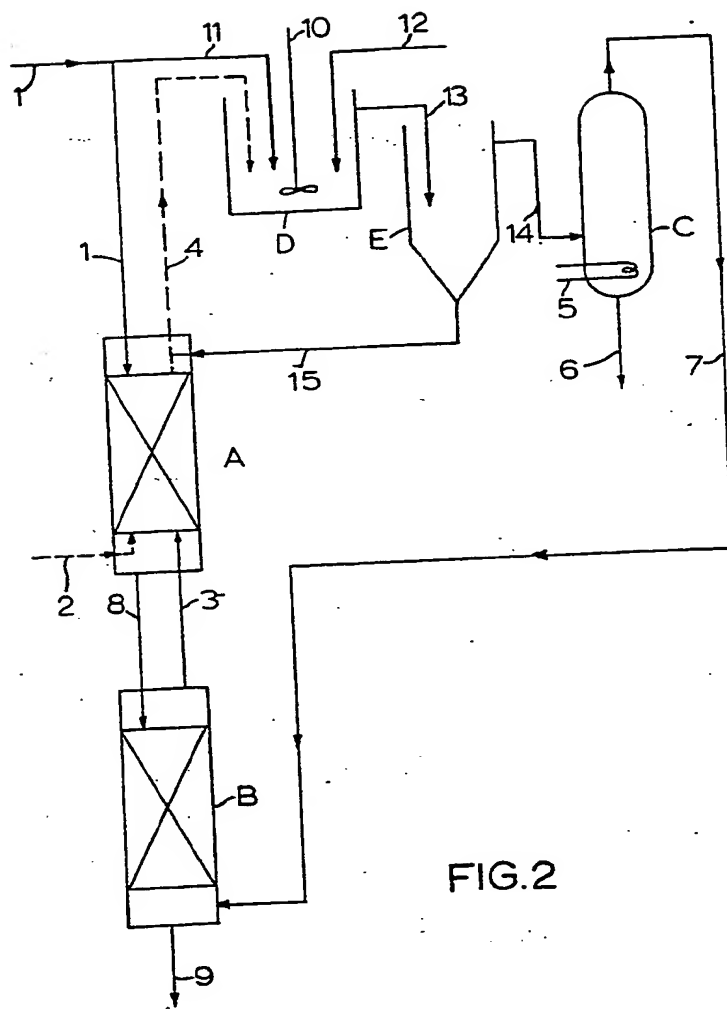


FIG.2

BEST AVAILABLE COPY



RNSDOC.ID: <GR 1138750A 1 >